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Acid corrosion of plain and reinforced concrete sewage systems

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ABSTRACT: The infrastructure of concrete sewage systems is affected notably by biogenic sulfuric acid attack, which causes rapid deterioration of each of its components. To provide a better understanding of this mechanism of damage, this paper reports on research carried out to study the response of the cementitious concrete matrix and the reinforcement steel under the attack of sulfuric acid. Concrete industrial pipes were cast using ordinary portland cement and pulverized fly ash, and specimens obtained from the mixes were left for several cycles in a solution of sulfuric acid at different pH. Experiments were carried out to assess the loss of weight and the electrical corrosion potential. Results showed that sulfuric acid attack can be considered a surface phenomenon, in which the acid attack destroys the cover of concrete before it reaches the reinforcement.

KEYWORDS: biogenic sulphuric acid attack (BSA), concrete pipes, concrete corrosion

1. INTRODUCTION

For more than two decades, deterioration of wastewater infrastructure due to biogenic sulphuric acid (BSA) has been a topic of intense debate by researchers. The result of extensive study of this topic led to the production of many design manuals which helped to reduce the risk of infrastructural damage [1, 2, 3, 4, 5]. The main internal chemical attack on concrete pipes is the result of biological conversion of H_2S to sulphuric acid in the presence of moisture. This mechanism is primarily responsible for corrosion of piping systems, sewerage systems and wastewater treatment plants.

BSA deterioration of wastewater infrastructure is related with the sulphur cycle in wastewater infrastructure. In a properly designed sewer, flow velocities maintain enough air to avoid loss of oxygen due to microbial activity. Under certain conditions, oxygen is consumed by some micro-organisms much faster than they can be replaced, changing from an aerobic to an anaerobic system (oxygen deficiency). This condition can occur in systems with low gravity speed and long retention times.

Under anaerobic conditions, certain bacteria (Desulfovibrio) reduce sulphates $SO^{=}$, (frequently present in wastewater) to sulphide ions $S^{=}$. The sulphide ions can combine with hydrogen ions to form hydrogen sulphide (H_2S) which remains partially dissolved in water. Under warm temperatures, the solubility of the wastewater changes, increasing the amount of gas that escapes to the available space contained within the pipe. The H_2S released is re-oxidized to H_2SO_4 (sulphuric acid) by an aerobic bacterium in the part of the tube that is not submerged. The bacterium responsible for this process is called "Thiobacillus Thiooxidante", also known as “Thiobacillus Concretivorus”. Hydrogen sulphide gas is not known to be aggressive to concrete, but it is toxic and produces foul odours. In contrast, H_2SO_4 produces a strong acid attack in the cement

matrix of concrete and in some limestone aggregates.

Portland cement is the major material used in the construction of sewage and drainage pipes and its derivatives are strongly alkaline (pH is usually above 12.5), so they are easily attacked by acid solutions. If the pH decreases, the balance in the cement matrix is changed and the hydrated components are essentially altered by decomposition of the electrolyte, resulting in severe degradation of the properties of the material. At pH values below 12.6, the portlandite is the first to go in solution. If the pH drops to values below the limits of stability of hydrated cement, calcium silicates, calcium aluminates, and hydrated calcium ferroaluminates react and release calcium, decomposing in an amorphous hydrogel. The result of acid attack is the formation of certain calcium salts and the formation of hydrogels of silicon, aluminium and ferric oxide.

The deterioration process of concrete when it is attacked by sulphuric acid can be generally divided in two parts. One corresponding to the reactions that occur when it reacts with calcium hydroxide $Ca(OH)_2$ and another for the reaction of the acid with calcium silicate hydrates (CSH gel).

Initially, when the pH of the cement matrix descends from its normal value (12.5-13) to a value of 12, calcium hydroxide is dissolved, later, when the pH drops in the range of 11.6 to 10.6, gypsum is formed from the dissolution of portlandite. On the other hand, when the pH drops to values less than 12.5, the CSH phase behaves unsteadily, showing cycles of dissolution and precipitation, where in the same way, gypsum is obtained.

$$\underset{\text{Porlandite}}{Ca(OH)_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O}$$

$$\underset{\text{C-S-H gel}}{3CaO \cdot SiO_2 \cdot 3H_2O} + H_2SO_4 \longrightarrow CaSO_4 \cdot 2H_2O + Si(OH)_4$$

Additionally to the mechanisms mentioned above, the formation of gypsum (calcium sulphate) causes expansion and softening of the hardened concrete when combined with the cement tricalcium aluminates.

Concrete pipes used in wastewater systems can be of plain concrete or can be steel reinforced. The use of steel in pipes depends among other factors, on the diameter. Usually, for pipes with diameters bigger than 0.60 m is common to have a sufficient number of longitudinal steel bars designed to withstand a combination of internal pressure and external loads. In a reinforced concrete pipe, like in any reinforced concrete structure, concrete provides a double protection to the steel. Firstly as a physical protection, separating the steel from direct contact with the external environment, and secondly, as a chemical protection afforded by the passive film surrounding the steel [6]. According to [7], this film may have resulted from the reaction of the steel surface oxidation products ($Fe(OH)_3$) with the cement calcium hydroxide $Ca(OH)_2$, forming calcium ferrate [$CaO.Fe_2O_3$].

Also there are two situations that might lead to the destruction of the steel passivating layer and produce steel corrosion. Firstly, a decrease in the alkalinity of the concrete as a result of the reaction with acidic substances and secondly, the presence of chloride ions in contact with the reinforcement. The reduction of pH allows the complete dissolution of the passivating layer and therefore leads to steel corrosion. In a reinforced concrete pipe under an active biogenic sulphuric acid attack it can be expected simultaneous damage on the concrete and on the steel reinforcement.

Whilst for concrete damage due to BSA there is a huge amount of literature available in form of journal papers, reports, and pipe design procedures; there is limited information on steel corrosion of reinforced concrete under sulphuric acidic environments. In order to provide better understanding of the mechanism of damage, this paper reports on a research carried out to study separately the response of the cementitious concrete matrix and the reinforcement steel under the attack of sulphuric acid. To achieve this, concrete real industrial pipes were cast using ordinary Portland cement and pulverized fly ash. Specimens obtained from the mixes cast

were left several cycles in solution of sulphuric acid at different pH and experiments were carried out to asses the loss of weight and the electrical corrosion potential.

2. EXPERIMENTAL

2.1 Materials

All tests were carried out on samples corresponding to four different mixes. High early strength Portland cement (OPC) was used as is normally employed in the manufacture of precast elements, and Colombian Pulverized fly ash was used in order to improve the performance of the mixtures. The Pulverized fly ash was replaced in a proportion of 17% respect to the cement contents. For all mixtures two different water binder ratios were used and their design was made according to the requirements of the concrete production in a precast factory. Siliceous coarse and fine aggregate from a quarry with angular rough particles were used. Table 1 shows the proportions of the materials employed.

All the materials were mixed mechanically in a concrete pipe precast factory. As the normal concrete pipe production needs mixes with very low slump due to the machine and concrete requirements, it was decided to keep fix the amount of water for all mixtures and increase the amount of cementitious material in order to change the water binder ratio. The equipment used gave to the mixes high energy compaction with a resulting good compactness

Table 1. Mix design

	Mixes			
MATERIAL	**O-53**	**O-45**	**OFA-53**	**OFA-45**
OPC [kg/m3]	326	384	271	319
P. Fly Ash [kg/m3]	0	0	55	65
Dry Coarse agg. [kg/m3]	798	777	789	767
Dry Fine agg. [kg/m3]	1024	998	1012	984
Water [l/m3]	173	173	173	173
Water/binder	0.53	0.45	0.53	0.45

2.2 Preparation of specimens

Two types of tests were carried out, one on plain concrete specimens and other on samples of reinforced concrete. The plain concrete specimens were obtained from the manufacture of pipes (40 cm in diameter, nominal thickness of 4.5 cm and without reinforcement). Once manufactured, the pipes were cured by water spray during the first three days. After curing, the pipes were cut to obtain specimens of 5cm x 5cm x 4.5cm nominal size. Figure 1 shows the preparation of the plain concrete samples.

The reinforced concrete samples were cast simultaneously with the pipes, using the same materials, but they were compacted manually on cylindrical plastic moulds of 5cm diameter and 10cm high with a 4 mm steel bar introduced in the middle of the sample. It was necessary to apply a superplastizer chemical admixture due to the low slump of the mixes and to compact the fresh samples with a vibrating table. Figure 2 shows the preparation of the reinforced samples.

2.3 Exposure conditions

After 28 days of casting, all the specimens were transferred to sulphuric acid environments in exposure solutions of very low pH (1.5), low pH (4.0) and neutral pH (7.0). The plain concrete tests were conducted with three replicates for each condition. For those, the level of deterioration of concrete was determined by the weight loss of material after drying and brushing the samples.

Additionally, for tests on reinforced concrete samples, two replicates were used for each condition. In these cylindrical specimens, direct contact was not allowed between the acid and the reinforcement bars. In order to achieve this, the bottom and the top of the samples were covered with an acid resistant epoxy material, so, the acid would have to penetrate through the porous matrix in order to reach the concrete. The level of deterioration of the steel was determined by an indirect measure consisting on the corrosion electric potential.

Figure 1. Preparation of plain concrete specimens

Figure 2. Reinforced concrete specimens

The specimens studied were immersed in tanks filled with their respective solutions of sulphuric acid and the pH was controlled at intervals of two days, time in which the pH increased about 15% through the release of alkalis and calcium from the concrete samples. Acid was added every two days while all the overall solutions were renewed every month. The control of the pH was achieved with a digital portable pH meter with automatic temperature compensation.

2.4 Experimental Methods

Compressive strength tests were carried out 28 days after casting, the procedure followed was the ASTM C39 [8] "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens".

The concrete alkalinity is described in literature as a design parameter proposed to quantify the BSA attack. It represents the total alkalinity of the cement bonded material, expressed as $CaCO_3$ equivalent and indicates the ability of concrete to resist an acidic environment. Due to the alkaline nature of cement, it tends to react with acidic environments, so the total alkalinity is a measure of the reactivity of a known mass of concrete [3].

The alkalinity test samples were obtained by drilling into the wall of each pipe and collecting the resulting dust. This powder was dried in an oven at a controlled temperature of 110 º C for 2 hours. The chemical procedure to calculate the alkalinity as a percentage was the following: approximately 1 gram of sample was added to 10 ml of distilled water. Subsequently, 40 ml of a 1 N solution of hydrochloric acid, HCl, was added. When the effervescence was over, the mixture was heated until boiling for 30 seconds before being cooled. Once the sample was cold, 50-100 ml of water was added and titrated with a 1 N solution of sodium hydroxide. The $CaCO_3$ was calculated according to equation 1.

$$CaCO_3.Equivalent[\%] = \frac{5[(ml.of.HCl) - (ml.of.NaOH)]}{[weigth of.the.sample]} \quad (1)$$

For evaluating the resistance of concrete exposed to sulphuric acid there is no standard criteria; however, the weight loss of the specimens is considered a good indicator [9]. Concrete specimens were immersed in acid solutions and every two weeks the samples were withdrawn from their respective tanks to be weighed with a precision analytical balance of 0.001g. Prior to weighing, the samples were introduced in an electric kiln at a temperature of 250 ºC for four hours and then brushed with a wire brush, making sure each side was brushed four times with the same pressure.

Removal of the weak reaction products from the surface of concrete was though the best way of simulating the erosion effects inside a pipe. Once the samples were weighed they were placed again in the respective acidic solutions.

The level of deterioration of the steel was determined by correlating the electrical potential of the reinforcement by using a standard reference electrode. The procedure followed was the ASTM C-876 [10]. The reference electrode in contact with the sample surface was connected

to the negative end of a voltmeter, while the reinforcement that was embedded within the concrete was connected to the positive end of the voltmeter. The contact between the concrete sample and the reference electrode was improved using a pre-wetted thin flat sponge. All measurements were made at the mid-height of the specimen and three readings were taken around the perimeter; the final value recorded was the average of the readings. Once the reinforced concrete specimens were immersed in their acid solutions, every two weeks the samples were withdrawn in order to take the potential readings. ASTM C-876 provided general guidelines for evaluating corrosion in concrete as outlined in Table 2. Note that the potentials are in respect to a reference electrode.

3. RESULTS AND DISCUSSION

3.1 Compressive strength and Calcium Carbonate Equivalent tests

Table 2. Probability of corrosion according to half-cell potential readings (ASTM C-876)

Half-cell potential reading vs. SCE	Corrosion activity
less negative than -0.200 V	90% probability of no corrosion
between -0.200 V and -0.350 V	an uncertain probability of corrosion
more negative than -0.350 V	90% probability of corrosion

Figure 3 shows the results of compressive strength and total alkalinity as $CaCO_3$ equivalent for all the mixes evaluated. As was expected, a decrease in the water to binder ratio produced an increase in the compressive strength. The samples added with fly ash showed a lower strength due probably to the slow hydration of this kind of admixture. Of the two variables studied (water to binder ratio and admixture replacement), the bigger difference on compressive strength was due to the presence of fly ash.

The fly ash samples showed a lower alkalinity than their similar. Due to the mixing requirement during casting, the water binder ratio was controlled adding more cementitious material to the mixtures and keeping the water content constant. This resulted in an important increase of the total alkalinity on the mixes with low water binder ratio.

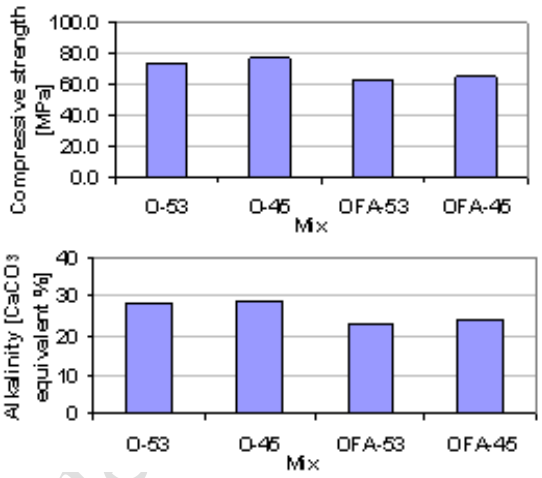

Figure 3. Concrete Compressive strength and total alkalinity

3.2 Visual observations

All plain concrete specimens before being immersed in the acid solutions had a similar physical appearance. There was a good compaction result of the mechanical fabrication of the pipes.

During the first 2 days of immersion a small change in colour was observed for all the specimens and for all the pH conditions. However, from the first week it was noticed in all specimens subjected to pH 1.5 the formation of a white layer that began growing around the surface of the samples. It is believed that this white substance is formed principally of gypsum. In the mixtures with just OPC the growth of that white layer was higher than for the samples using fly ash. Before the first weighing all the specimens were photographed and are shown in figure 4 where can be seen the differences for the pH conditions. No significant difference was noted between the specimens made using different water binder ratios.

Figure 4. All samples after the second week of sulphuric acid contact

From the third week of test, the specimens immersed in a pH of 1.5 started to lose the concrete that covers the aggregate and the white colour was accentuated. The samples immersed in intermediate and neutral pH solutions showed no major changes than the observed during the first week. From week 5 there was a progressive deterioration of the material in the samples under 1.5 pH. The cement matrix surface was attacked allowing the aggregate free, accelerating weight loss. The specimens using fly ash showed fewer differences in colour than the just OPC. The loss of material at this stage was much more noticeable for samples without fly ash. Contrary to the expectation, some of the samples with low water cement ratio (0.45) showed more surface damage than the specimens with high water binder ratio. This phenomenon is discussed later in detail.

In the eighth and ninth weeks of immersion, the deterioration for samples under very low pH (1.5) was strong. Initially, the specimens had right angles at their corners; however, after several cycles the size of the specimens was reduced significantly for all mixtures. Samples with fly ash had a better physical appearance than the OPC samples. The weight of loss for the samples under conditions of high acidity was principally due to the loss of the aggregate that forms the matrix of concrete. While the cement matrix is altered and changed because of its reaction with the acid, the aggregate did not present any type of attack. The loss of adhesion between paste and aggregate is primarily responsible for the loss of weight. For mixtures under low pH (4) the surface deterioration increases but the degradation rates were relatively low. Although the loss of material was visually noticeable, the occurrence of the white layer was not noticed. In figure 5 can be seen some specimens in the 9 week for all the pH environments.

When all the immersion cycles (90 days) were completed, a specimen (under very low pH) was cut to determine the depth of acid penetration. It was found that the material had been degraded only superficially. No evidence was found of the presence of acid different from the outer surface of the samples. Figure 6 shows the external and internal surfaces of a specimen after 90 days of acid attack for a very low pH.

Figure 5. a) Specimen OFA-53 (pH=7) week 9; b) specimen OFA-53 (pH=4) week 9; c) specimen OFA-53 (pH=1.5) week 9; d) Loss of aggregate due to the sulphuric acid attack

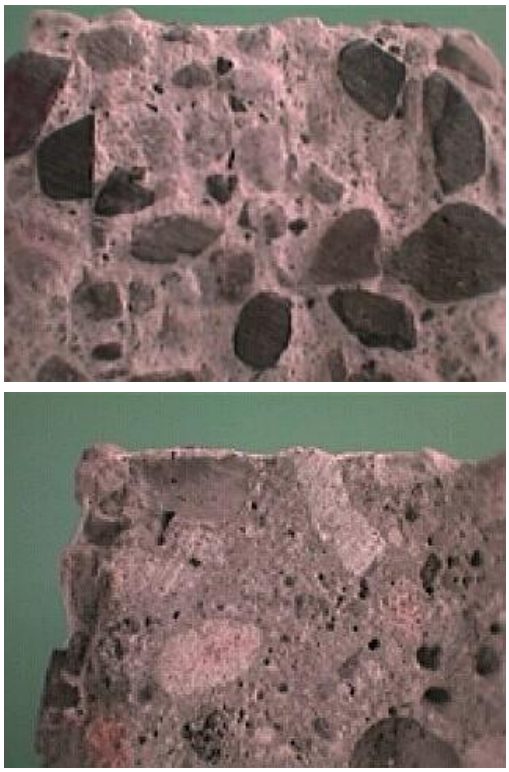

Figure 6. Samples after 90 days of sulphuric acid attack, a) Surface area attacked by the acid; b) Internal zone unchanged

3.3 Weight loss

Figure 7 shows the evolution of the weight loss for each one of the mixtures in each pH. The specimens subjected to pH levels of 1.5 had a weight loss between 9 and 12%, while for pH levels of 4, the weight loss occurred between 1 and 2%. For samples immersed in neutral pH conditions, the weight loss was between 0 and 1%. In some specimens submerged under pH of 1.5 and 4, weight gain occurred during the first days of immersion. This weight increase could happen because in the reaction between sulphuric acid and concrete the calcium hydroxide results in calcium sulphate, which in turn becomes calcium sulfoaluminate. This reaction produces a decrease in density and an increase in volume. If the increase in volume is greater than the loss of density, weight increase could occur.

The behaviour of the specimens under sulphuric acid attack at pH of 1,5 and 4 was clearly influenced by the presence of fly ash. Under these acidic conditions the combination of the chemical and physical response of concrete gave some level of strength against the aggressive environment. In contrast, for samples subjected to neutral pH solutions the weight loss was more correlated with the mechanical strength of the mixtures. This was expected because under this condition the mechanisms of deterioration had a physical rather a chemical component.

Contrary to what was expected, only for very low acidic environments, tests showed that mixtures with higher water binder ratios showed a better behaviour against acid attack. This could be attributed to several reasons among which include parameters such as the amount of cementitious materials and the type of test performed. The mix design used, as a control parameter for all the samples, contained the same amount of water. In order to decrease the water binder from 0.53 to 0.45 for any mixture, the requirement was to increase the amount of cementitious material in 58 kg per cubic meter of concrete. As the cement is highly alkaline, this leads to a corresponding increase in the alkalinity of concrete samples.

As stated earlier, the alkalinity is defined as the property of the material to react with acid to neutralize it and form water. The result of tests to determine the behaviour of concrete in acid environments is dependent on the characteristics of the test. Hence, contradictory results can be obtained as a result of differences in tests. In a concrete pipe at normal operating conditions, the volumes of sulphuric acid are very small relative to the volumes of concrete present in the pipeline. This explains why the alkalinity of the concrete takes on a very important role. While more alkaline (higher cement content) is contained in the pipe, more quantities of acid could be neutralized. In contrast, in a chemical laboratory test such as conducted in this research, in which specimens have relatively low volumes of concrete and are embedded in large volumes of sulphuric acid, the alkalinity of the mixture does not provide any advantage. Due to the high ratio volume of acid / alkalinity of the sample, the

amount of acid neutralized by the alkalinity of the sample is minimal. In that way, it is not considered as an advantage for to have high alkalinity in tests such as the one conducted in this study. A similar discussion was presented by Fattuhi and Hughes [11].

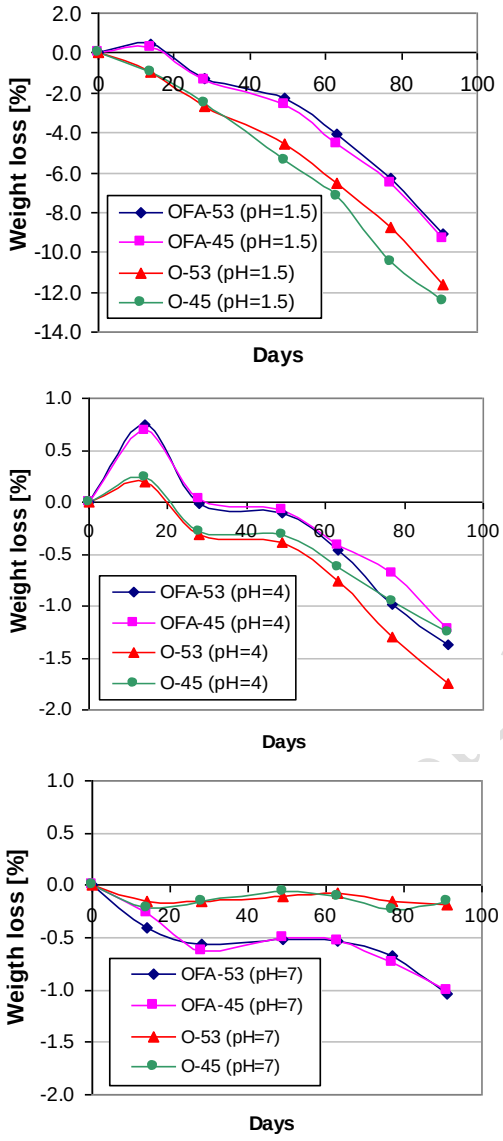

Figure 7. Weight loss for different environments

3.4 Corrosion potential

Figure 8 shows results for all the samples under the different acid solutions. The specimens immersed in a solution of H_2SO_4 with a pH of 1.5 maintained throughout all the duration of the experiments a reference potential below 250 mV, only a few points fell in the uncertain zone of 250-350 millivolts. In accordance with the potential taken, reinforcement embedded within the concrete specimens did not show electrical activity that could degenerate into electrochemical corrosion. It can be stated that the steel was not aware of the concrete acid attack. The behaviour of the reinforced concrete specimens in pH 4 and neutral conditions gave the same results as for the condition of pH 1.5. All potentials measured were in the safety range for the phenomenon of corrosion of steel.

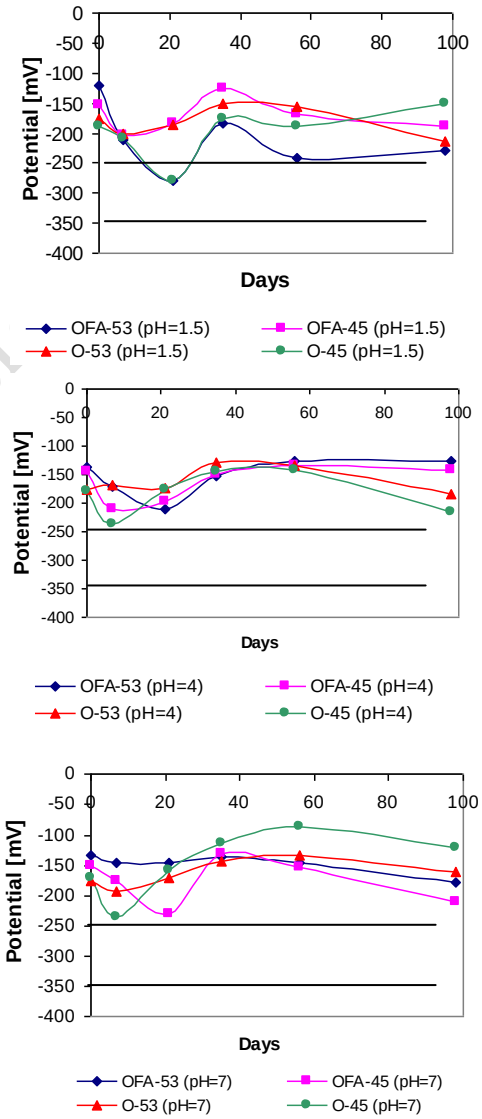

Figure 8. Corrosion potential

The absence of corrosion on the steel was mainly because the sulphuric acid attack is a totally superficial phenomenon. Its penetration into the

concrete occurs simultaneously with the destruction of the most superficial layers of the specimen. Unlike the chloride attack that is well documented in the literature, the acid penetrates and reacts with concrete simultaneously, so the penetration away from the affected area is very small. Conversely, in the chloride attack, the ions penetrate the concrete matrix without producing harmful reactions to the concrete. Figure 9 shows a cylinder cross section of a reinforced concrete after completion of the cycles of acid attack.

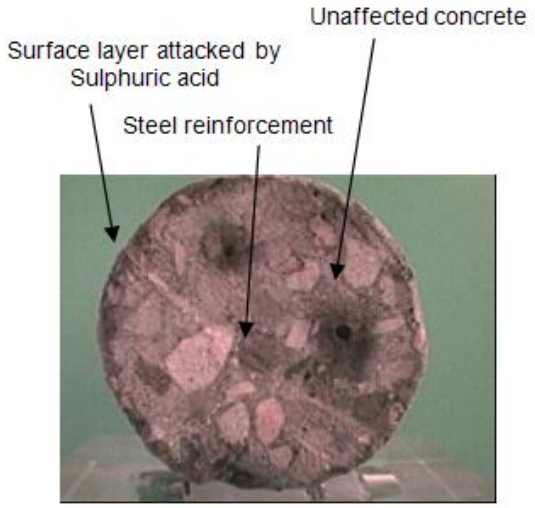

Figure 9. Cross section of a reinforced specimen at the end of the test

4. CONCLUSIONS

- It is essential to interpret the research results according to the type of test conducted. Although the chemical tests carried out, under very low pH, do not reproduce in a real life scenario the kinetics of the generation of sulphuric acid inside the pipe, the results provides understanding and assessment of the behaviour of concrete and its components under acidic environments.

- The concrete specimens using fly ash showed a better performance against the sulphuric acid attack than those without this admixture. Under high and intermediate concentrations of acid, samples using fly ash as cement replacement showed a much lower weight loss than their counterparts.

- Sulphuric acid attack can be considered a surface phenomenon, in which the damage occurs from the outside. As the acid comes into contact with concrete it reacts with the surface that has interaction, producing damage and at the same time penetrating the material. The effects of the acid aggression on the concrete are only noticed in areas of direct contact with the acid. Unlike other phenomena of deterioration such as carbonation or chloride ions attack, in which substances penetrate the porous matrix of concrete without strong and harmful interactions with the concrete matrix, the sulphuric acid attack destroys the concrete cover of the structure firstly in order to reach the reinforcement and corrode it electrochemically.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] **U.S. ENVIRONMENTAL PROTECTION AGENCY**, Process design manual for sulphide control in sanitary sewerage systems, Technology Transfer Office, 1974.

[2] **US ENVIRONMENTAL PROTECTION AGENCY**, Design Manual: Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants, (EPA) 625185018, 1985.

[3] **FREDERICK R MCLAREN**, Design manual sulphide and corrosion prediction and control, American concrete pipe association, 1985.

[4] **ASCE**, Sulphide in Wastewater Collection and Treatment Systems, ASCE Manual No 69, New York, NY, 1989.

[5] **THISTLETHWAYTE, D.K.B**, The Control of Sulphides in sewerage Systems, Ann Arbor Science, Ann Arbor- MI, 1972.

[6] **RED DURAR**, Manual de inspección, evaluación, y diagnostico de corrosión en estructuras de hormigón Armado, Cyted, 1998.

[7] **JONES, D. A.**, Principles and Prevention of Corrosion, Prentice Hall, Upper Saddle NJ, 1996.

[8] **AMERICAN SOCIETY FOR TESTING AND MATERIALS**, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM-C39, ASTM International West Conshohocken, Pennsylvania, 2009.

[9] **K. TAMIMI**, High-performance concrete mix for an optimum protection in acidic conditions, Materials and Structures Vol. 30, pp 188-191, 1997.

[10] **AMERICAN SOCIETY FOR TESTING AND MATERIALS**, Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete, ASTM-C876, ASTM International West Conshohocken, Pennsylvania, 1991.

[11] **FATTUHI N. I. AND HUGHES B. P.**, Ordinary Portland cement Mixes With Selected Admixtures Subjected to Sulphuric Acid Attack, Materials Journal, Vol 85, Issue 6, 1988.